

[54] AZO DYES HAVING A 3-HALO-4-CYANO OR ACYL-6-HYDROXYPYRIDONE-2 COUPLING COMPONENT RADICAL

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[63] Continuation of Ser. No. 253,410, May 15, 1972, abandoned.

Foreign Application Priority Data

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[51] Int. Cl.² C09B 29/36; C09B 43/00

[58] Field of Search 260/156, 155

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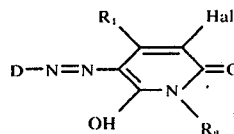
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Primary Examiner—Charles F. Warren
 Attorney, Agent, or Firm—Gerald D. Sharkin; Richard E. Vila; Melvyn M. Kassenoff

[57] **ABSTRACT**

The invention provides novel disperse dyes of formula I,



in which

D signifies the radical of a diazo component,

Hal signifies chlorine or bromine,

R₂ signifies hydrogen, unsubstituted or substituted amino, or an unsubstituted or substituted hydrocarbon radical which may contain hetero atoms,

and

R₁ signifies cyano or a radical —COOR₃ or —CONR₄R₅, in which R₃ signifies unsubstituted or substituted alkyl or phenyl, R₄ signifies hydrogen, unsubstituted or substituted amino, or an unsubstituted or substituted hydrocarbon radical which may contain hetero atoms,

and R₅ signifies hydrogen or unsubstituted or substituted alkyl or phenyl,

provided that the compounds contain no sulphonic acid radicals.

These dyes are useful for dyeing and printing synthetic and semisynthetic high molecular weight hydrophobic fibers such as aromatic polyesters, synthetic polyamides, secondary cellulose acetate and cellulose triacetate. The dyeings are fast to light, thermofixation, sublimation, pleating, wet treatments, dry cleaning, lubricants, rubbing, cross-dyeing, ozone, gas fumes and chlorine.

26 Claims, No Drawings

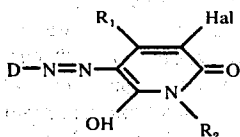
AZO DYES HAVING A 3-HALO-4-CYANO OR ACYL-6-HYDROXYPYRIDONE-2 COUPLING COMPONENT RADICAL

This application is a continuation of application Ser. No. 253,410, filed May 15, 1972 and now abandoned.

IMPROVEMENTS IN OR RELATING TO ORGANIC COMPOUNDS

This invention relates to azo dyes of low water solubility and in which the coupling component is a 5-halo-citrazinic acid derivative.

More particularly, this invention provides compounds of formula I,



in which

D signifies the radical of a diazo component,

Hal signifies chlorine or bromine;

R₂ signifies hydrogen, unsubstituted or substituted amino, or an unsubstituted or substituted hydrocarbon radical which may contain hetero atoms, and

R₁ signifies cyano or a radical -COOR₃ or -CONR₄R₅, in which R₃ signifies unsubstituted or substituted alkyl or phenyl, R₄ signifies hydrogen, unsubstituted or substituted amino, or an unsubstituted or substituted hydrocarbon radical which may contain hetero atoms,

and R₅ signifies hydrogen or unsubstituted or substituted alkyl or phenyl, provided that the compounds contain no sulphonic acid radicals.

Suitable diazo components include aromatic hydrocarbon, radicals and heterocyclic radicals of aromatic character, such as pyridyl, thienyl, thiazolyl, benzothiazolyl, benzisothiazolyl, thiadiazolyl, imidazolyl, triazolyl, quinolyl, isoquinolyl, naphthyl and, in particular, phenyl. These radicals may bear substituents conventional in azo dyes, for example halogen, particularly chlorine or bromine, hydroxyl, cyano, thiocyno, nitro, acyl, acyloxy or acylamino, or alkyl, alkoxy, phenyl, phenoxy, alkylmercapto or phenylmercapto which may be unsubstituted or substituted.

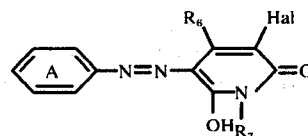
Where R₂ or R₄ signify substituted amino, the amino radical may for example be substituted by one or two unsubstituted or substituted alkyl radicals, by an unsubstituted or substituted phenyl radical, by a heterocyclic radical such as those mentioned above for the diazo component or as morpholino, piperidino or sulpholan radicals, or by two different substituents, e.g. one unsubstituted or substituted alkyl substituent and one phenyl substituent. Preferred acyl substituents include those of formula R-Y or R'-Z, in which R signifies an unsubstituted or substituted hydrocarbon radical which may contain hetero atoms, preferably unsubstituted or substituted alkyl or phenyl, Y signifies -O-CO- or -SO₂-, R' signifies hydrogen or R, and Z signifies -CO-, -NR''CO- or -NR''SO₂- in which R'' signifies hydrogen or R.

Suitable hydrocarbon radicals include, in particular, alkyl, phenyl, cycloalkyl, such as cyclohexyl, and unsaturated radicals, such as allyl.

Suitable hydrocarbon radicals containing hetero atoms include the heterocyclic radicals mentioned above in connection with the diazo component and also morpholino, piperidino and sulpholan radicals. Suitable substituents on any substituted such hydrocarbon radicals include those mentioned above in connection with the diazo component.

As used herein, the terms "alkyl" and "alkoxy" mean, unless otherwise indicated, alkyl or alkoxy radicals containing 1 to 6, preferably 1 to 4 carbon atoms. Suitable substituents on any substituted such radical, and indeed on any other substituted radical, include those mentioned above in connection with the diazo component.

The preferred compounds of formula I, are those of formula Ia,



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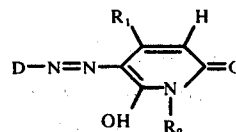
in which ring A may bear one or more substituents selected from chlorine, bromine, nitro, methyl, methoxy, phenyl, phenoxy, chlorophenoxy, bromophenoxy, acetyl, phenoxysulphonyl, phenylsulphonyloxy, dimethylaminocarbonyloxy (dimethylcarbamyloxy) or dimethylaminosulphonyloxy (dimethylsulfamoyloxy), or alkoxy carbonyl in which the alkoxy group contains 1 to 4 carbon atoms, or benzoyl,

R₆ signifies cyano, alkoxy carbonyl, in which the alkoxy radical contains 1 to 4 carbon atoms, phenoxy carbonyl, aminocarbonyl (carbamoyl), alkylaminocarbonyl or dialkylaminocarbonyl in which each alkyl radical contains 1 to 4 carbon atoms, phenylaminocarbonyl, or methoxyalkylaminocarbonyl, in which the alkyl radical contains 1 to 3 carbon atoms,

R₇ signifies hydrogen, phenyl, sulpholyl, N-piperidyl, dimethylamino, unsubstituted alkyl of 1 to 3 carbon atoms, or alkyl of 1 to 3 carbon atoms substituted by methoxy, hydroxyl, cyano, acetylamino (acetamido), phenyl or alkoxy carbonyl, in which the alkoxy radical contains 1 or 2 carbon atoms,

and Hal is as defined above.

The compounds of formula I may, in accordance with the invention, be produced by chlorinating or brominating a compound of formula II,



in which D, R₁ and R₂ are as defined above.

The process is suitably effected in an inert organic solvent, for example a substituted benzene, e.g. nitrobenzene. The process is conveniently carried out by dissolving or suspending the compound of formula II in the solvent, and bubbling chlorine through or adding

bromine to the resulting mixture. Alternatively, the chlorine or bromine may be dissolved in a solvent before addition, or the chlorination or bromination may be effected using a chlorine or bromine donor, such as an amide or imide of an N-chloric or N-bromic acid, e.g., N-chloro- or bromo-succinimide, or chloro- or bromophthalimide. Conveniently, the process is effected at a temperature of from 20° to 70° C.

The resulting compounds of formula I may be isolated and purified using conventional techniques.

The compounds of formula II are known or may be prepared in known manner from available materials, for example by conventional coupling of the appropriate diazo and coupling components.

The compounds of formula I may be formulated into dyeing preparations before use in conventional manner, for example by grinding in the presence of dispersing agents and/or fillers, followed by vacuum or atomiser drying if dry products are required. After addition of a suitable quantity of water, the preparations can be applied by known exhaust dyeing, pad dyeing or printing methods (see, for example, French Pat. 1,445,371) at long to short liquor ratios.

The dyes of the invention are suitable for dyeing and printing synthetic and semisynthetic, high molecular weight organic fibres of hydrophobic character, in loose form, as yarn and in other textile forms. From aqueous dispersion they build up well on textile substrates of such fibres. They are particularly suitable for dyeing and printing linear aromatic polyester, synthetic polyamide, secondary cellulose acetate and cellulose triacetate fibres.

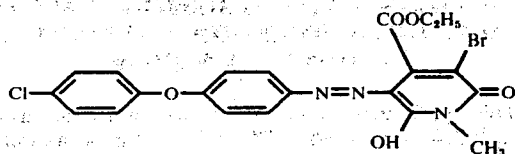
The dyeings obtained show good all-round fastness properties, for example with respect to light, thermofixation, sublimation, pleating, wet treatments, such as water, washing, sea water, perspiration, solvents and dry cleaning, and to lubricants, rubbing, cross-dyeing, ozone, gas fumes and chlorine. The dyeings are stable under the conditions of the pre-cure and post-cure permanent press finishing processes and to soil release finishes. Their dischargeability, resistance to reducing action in dyeing with wool and reserve of wool and cotton are also noteworthy.

The new dyes possess, in particular, noteworthy light and sublimation fastness properties and tinctorial strength in relation to similar known dyes.

As will be appreciated, the compounds of formula I, in which R₂ is hydrogen exhibit keto-enol type tautomerism. It is noted that the invention extends to all tautomeric forms. In the following Examples, the parts and percentages are by weight and the temperatures in degrees Centigrade.

EXAMPLE 1

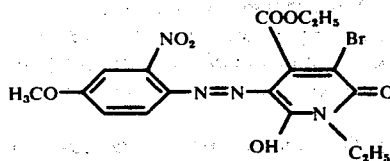
42.8 Parts of 1-methyl-3-[4'-(4''-chlorophenoxy)-phenylazo]-citrazinic acid ethyl ester are stirred into 600 parts of nitrobenzene at room temperature. Over the course of 1 hour, a solution of 16 parts of bromine in 120 parts of nitrobenzene is added, the temperature being kept between about 20° and 25° during this time. After addition, the temperature is increased to 60° and the reaction run for 1 hour at this temperature with stirring. On cooling, the dye of the formula



which is precipitated in insoluble form, is isolated by filtration and dried. After conversion into finely divided powder form, this dye is applicable to polyester fibres, on which it builds up to heavy depths and gives fast yellow dyeings.

EXAMPLE 2

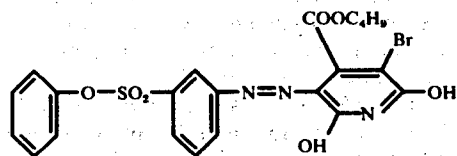
71.8 Parts of N-ethyl-3-(2'-nitro-4'-methoxyphenylazo)-citrazinic acid ethyl ester are stirred into 1200 parts of nitrobenzene. A solution of 30 parts of bromine in 360 parts of nitrobenzene is allowed to flow in gradually over 1 hour at room temperature. Subsequently the mixture is raised to 60° and reacted for 1 hour at this temperature with stirring. The dye formed, which has the formula



settles out from the cooling reaction medium and is isolated by filtration. It is worked up in a finely divided form, in which it dyes polyester textiles in fast yellow-orange shades.

EXAMPLE 3

A solution of 14 parts of bromine in 120 parts of nitrobenzene is allowed to flow slowly at room temperature into a suspension of 39.5 parts of 3-[3'-(phenoxysulphonyl)-phenylazo]-citrazinic acid n-butyl ester in 600 parts of nitrobenzene. The temperature is increased to 60°, with stirring, and held at this point for 1 hour, with continued stirring. Following cooling and filtration, the dye of the formula

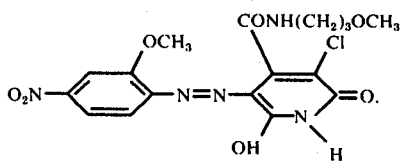


is obtained. It is converted into finely divided form for application to polyester fibres, on which it gives fast dyeings of greenish yellow shade.

EXAMPLE 4

A suspension of 70 parts of 3-(2'-methoxy-4'-nitrophenylazo)-citrazinic acid-(γ-methoxy)-propylamide in 1000 parts of nitrobenzene is prepared. Over the course of 2 hours, 12.3 parts of chlorine, previously liquefied in a cold bath, are evaporated into the suspension. The mixture is then raised to 60° and reacted for 1 hour at this temperature with stirring. The mixture is

then evaporated to about one half of its initial volume and cooled. The crystalline dye of the formula



settles out and is isolated by filtration. In finely divided form, it dyes polyester fibres in fast yellow shades.

The follow table indicates further dyes of formula I, stated above, which are produced in manner described in the preceding Examples.

TABLE

Exp. No.	D - NH ₂	R ₁	R ₂	Hal	Shade on polyester fibre
5	2-Chloro-4-nitroaniline	-COOC ₂ H ₅	H	Cl	yellow
6	"	-CN	-CH ₂ C ₆ H ₅	Cl	"
7	β-Naphthylamine	-COOC ₂ H ₅	-CH ₃	Br	"
8	2-Aminobenzothiazole	-COOC ₂ H ₅	-C ₆ H ₅	Br	orange
9	2-Methoxy-4-nitroaniline	-CONHC ₂ H ₅	-CH ₂ CH ₂ CH ₂ OCH ₃	Cl	reddish yellow
10	2-Aminothiazole	-COOC ₂ H ₅	-CH ₂ CH ₂ OH	Br	"
11	4-Ethoxycarbonylaminoaniline	-CONH ₂	-CH ₂ CH ₂ CN	Br	"
12	2,5-Dichloroaniline	-CONHC ₂ H ₅		Br	"
13	2,5-Dichloroaniline	-CON(CH ₃) ₂	-C ₆ H ₅	Br	yellow
14	2-Phenylsulphonyloxyaniline	-COOC ₂ H ₅	-N(CH ₃) ₂	Br	"
15	2-Methyl-4-nitroaniline	-CONHC ₆ H ₅	-CH ₃	Cl	"
16	4-(4'-Chlorophenoxy)-aniline	-COOC ₆ H ₅	H	Br	yellow
17	2,4-Dichloroaniline	-CN	-CH ₃	Cl	"
18	2-Nitro-4-chloroaniline	-CON(C ₂ H ₅) ₂	"	Br	reddish yellow
19	4-Phenylaniline	-COOC ₂ H ₅	-CH ₂ CH ₂ COOC ₂ H ₅	Br	yellow
20	4-Nitroaniline	-COOC ₆ H ₅	-C ₆ H ₅	Br	"
21	3-Dimethylaminosulphonyloxyaniline	-COOC ₂ H ₅	H	Br	"
22	3-Aminopyridine	-COOC ₂ H ₅	H	Cl	"
23	2,6-Dichloro-4-nitroaniline	-CONHCH ₃	-CH ₂ CH ₂ CH ₂ OCH ₃	Br	"
24	4-Aminoazobenzene	-CONC ₂ H ₅	-CH ₂ CH ₂ CH ₂ OCH ₃	Cl	orange
25	2-Chloro-4-nitroaniline	-COOC ₂ H ₅ CH ₃		Cl	yellow
26	4-Dimethylaminocarbonyloxyaniline	-COOCH ₃	-CH ₂ CH ₂ NHCOCH ₃	Br	"
27	4-(4'-Chlorophenoxy)-aniline	-CONHC ₆ H ₅	H	Br	"
28	4-(4'-Bromophenoxy)-aniline	"	H	Br	"
29	4-Phenoxyaniline	"	H	Br	"
30	4-Phenylsulphonyloxyaniline	-COOC ₂ H ₅	H	Br	yellow
31	"	"	"	Cl	"
32	4-Benzoylaniline	"	"	Cl	"
33	"	"	"	Br	"
34	2-Methoxy-4-nitroaniline	-CONHCH ₃	CH ₃	Br	"
35	"	"	"	Cl	"
36	4-Ethoxycarbonylaniline	-CONH(CH ₂) ₃ OCH ₃	-(CH ₂) ₃ OCH ₃	Cl	"
37	"	"	"	Br	"
38	2,6-Dichloro-4-nitroaniline	-COO(CH ₂) ₃ CH ₃	H	Cl	"
39	"	"	"	Br	"
40	2-Chloro-4-n-butoxycarbonylaniline	-COO-n-C ₄ H ₉	H	Br	"
41	"	"	"	Cl	"
42	4-ethoxycarbonylaniline	CONH(CH ₂) ₃ OCH ₃	(CH ₂) ₃ OH	Cl	"
43	4-ethoxycarbonylaniline	CONH(CH ₂) ₃ OCH ₃	(CH ₂) ₃ OH	Br	"

wherein

D is phenyl, naphthyl, pyridyl, thienyl, thiazolyl, benzothiazolyl, benzoisothiazolyl, thiadiazolyl, imidazolyl, triazolyl, quinolyl or isoquinolyl, or a substituted derivative thereof,

wherein each substituent of each substituted derivative is independently halo, hydroxy, cyano, thiocyno, nitro, acyl, acyloxy, acylamino, alkyl, alkoxy, phenyl, phenoxy, phenoxy substituted by chlorine or bromine, phenoxy sulfonyl, alkylmercapto, phenylmercapto or phenylazo,

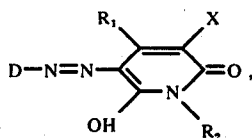
R₁ is cyano, -COOR₃ or -CONR₄R₅,

wherein R₃ is alkyl or phenyl,

R₄ is hydrogen, alkyl, alkoxyalkyl, phenyl, amino, alkylamino, dialkylamino, phenylamino, N-alkyl-N-phenylamino, morpholino, piperidino or sulfo-

What is claimed is:

1. A compound of the formula



lyl, and

60 R₅ is hydrogen, alkyl or phenyl,

R₂ is hydrogen, alkyl, alkyl substituted by alkoxy, hydroxy, cyano, alkylcarbonylamino, phenyl or alkoxy carbonyl, phenyl, amino, alkylamino, dialkylamino, phenylamino, N-alkyl-N-phenylamino, morpholino, piperidino or sulfolyl, and

65 X is chloro or bromo,

wherein each acyl and acyl radical of each acyloxy and acylamino is independently R-Y- or R'-Z-,

wherein

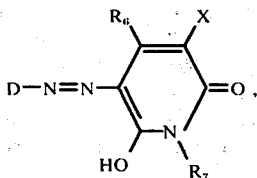
R is alkyl or phenyl,

Y is $-\text{OCO}-$ or $-\text{SO}_2-$,

R' is hydrogen, alkyl or phenyl, and

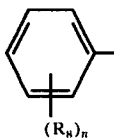
Z is $-\text{CO}-$, $-\text{NR}'-\text{CO}-$ or $-\text{NR}'\text{SO}_2-$, and each alkyl, alkoxy, alkyl moiety and alkoxy moiety independently has 1 to 6 carbon atoms.

2. A compound according to claim 1 having the formula



wherein

D is



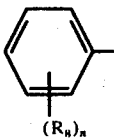
, 2-naphthyl, 2-benzothiazolyl, 2-thiazolyl or 3-pyridyl, wherein each R_8 is independently chloro, bromo, nitro, methyl, methoxy, phenyl, phenoxy, chlorophenoxy, bromophenoxy, acetyl, phenoxy-sulfonyl, phenylsulfonyloxy, dimethylcarbamoyloxy, dimethylsulfamoyloxy, benzoyl, ethoxycarbonylamino, phenylazo or alkoxy carbonyl wherein the alkoxy radical has 1 to 4 carbon atoms, and n is 0 to 3,

R_6 is cyano, alkoxy carbonyl, phenoxy carbonyl, carbamoyl, alkyl carbamoyl, dialkyl carbamoyl, phenyl carbamoyl or methoxy alkyl carbamoyl, wherein the alkyl radical of alkyl carbamoyl, each alkyl radical of dialkyl carbamoyl and the alkoxy radical of alkoxy carbonyl has 1 to 4 carbon atoms and the alkyl radical of methoxy alkyl carbamoyl has 1 to 3 carbon atoms,

R_7 is hydrogen, phenyl, sulfolyl, N-piperidino, dimethylamino, alkyl of 1 to 3 carbon atoms or alkyl of 1 to 3 carbon atoms substituted by methoxy, hydroxy, cyano, acetamido, phenyl or alkoxy carbonyl wherein the alkoxy radical has 1 or 2 carbon atoms, and

X is chloro or bromo.

3. A compound according to claim 2 wherein D is



4. A compound according to claim 3 wherein n is 1 to 3.

5. A compound according to claim 3 wherein each R_8 is independently chloro, bromo, nitro, methyl,

methoxy, phenyl, phenoxy, chlorophenoxy, bromophenoxy, acetyl, phenoxy sulfonyl, phenyl sulfonyloxy, dimethyl carbamoyloxy, dimethyl sulfamoyloxy, benzoyl or alkoxy carbonyl wherein the alkoxy radical has 1 to 4 carbon atoms.

6. A compound according to claim 5 wherein n is 1 to 3.

7. A compound according to claim 5

wherein R_6 is alkoxy carbonyl, alkyl carbamoyl or methoxy alkyl carbamoyl,

wherein the alkoxy radical of alkoxy carbonyl and the alkyl radical of alkyl carbamoyl have 1 to 4 carbon atoms and the alkyl radical of methoxy alkyl carbamoyl has 1 to 3 carbon atoms, and R_7 is hydrogen or alkyl of 1 to 3 carbon atoms.

8. A compound according to claim 7

wherein each R_8 is independently chloro, nitro, methyl, methoxy, chlorophenoxy, phenoxy sulfonyl, phenyl sulfonyloxy, dimethyl sulfamoyloxy, benzoyl or alkoxy carbonyl wherein the alkoxy radical has 1 to 4 carbon atoms, and n is 1 to 3.

9. A compound according to claim 7

wherein

R_6 is alkoxy carbonyl wherein the alkoxy radical has 1 to 4 carbon atoms, and

X is bromo.

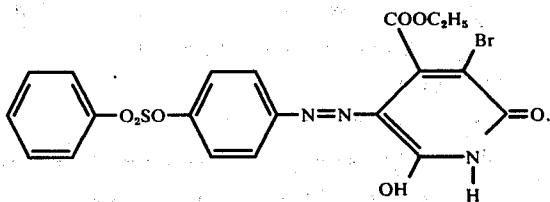
10. A compound according to claim 9

wherein

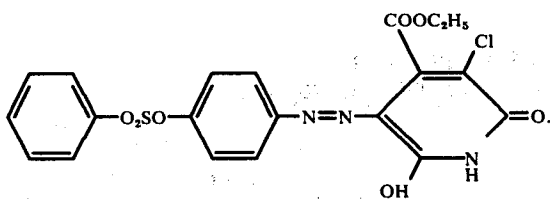
each R_8 is independently chloro, nitro, methoxy, chlorophenoxy, phenoxy sulfonyl, phenyl sulfonyloxy, dimethyl sulfamoyloxy, benzoyl or alkoxy carbonyl wherein the alkoxy radical has 1 to 4 carbon atoms, and

n is 1 to 3.

11. The compound according to claim 6 having the formula

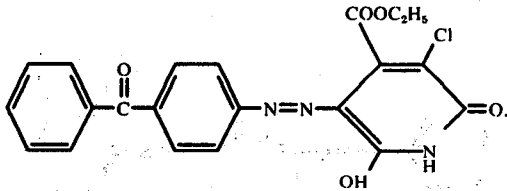


12. The compound according to claim 6 having the formula

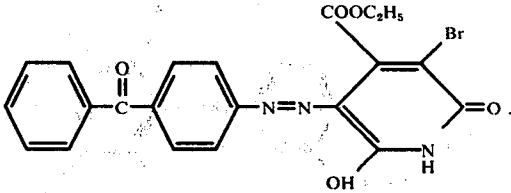


13. The compound according to claim 6 having the formula

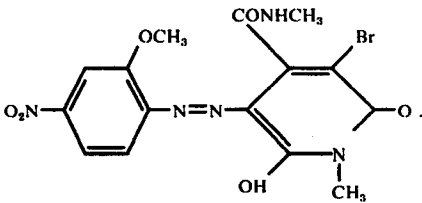
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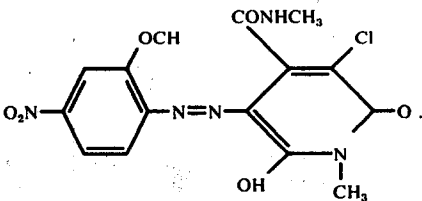
14. The compound according to claim 6 having the formula



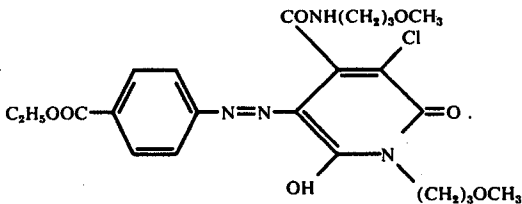
15. The compound according to claim 6 having the formula



16. The compound according to claim 6 having the formula

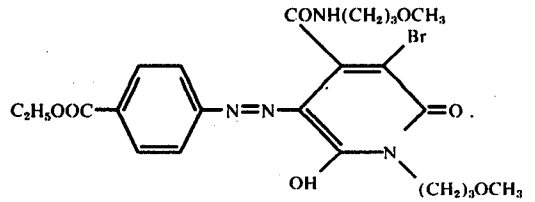


17. The compound according to claim 6 having the formula

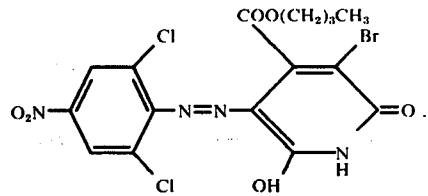


18. The compound according to claim 6 having the formula

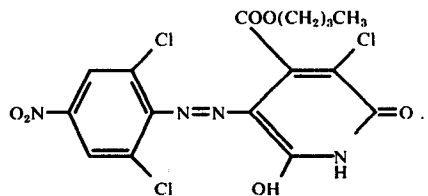
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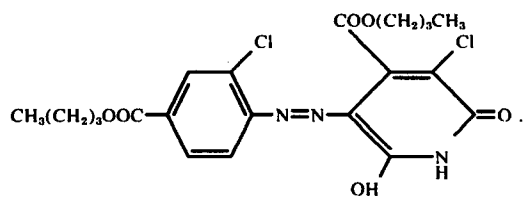
19. The compound according to claim 6 having the formula



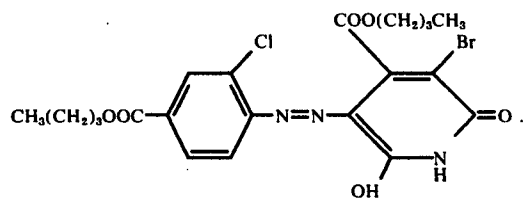
20. The compound according to claim 6 having the formula



21. The compound according to claim 6 having the formula

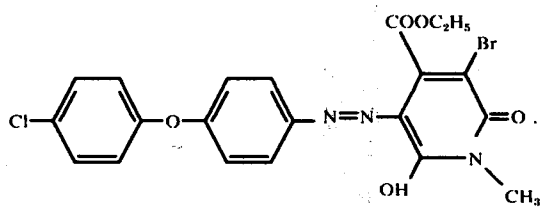


22. The compound according to claim 6 having the formula

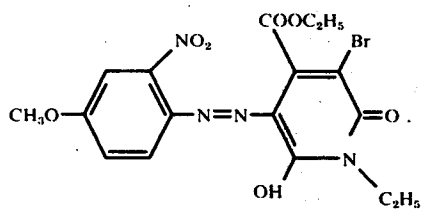


23. The compound according to claim 6 having the formula

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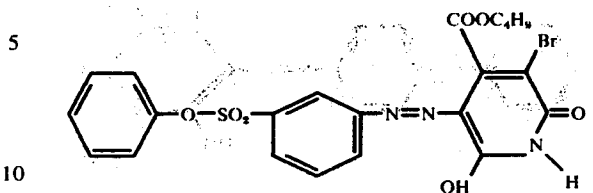


24. The compound according to claim 6 having the formula

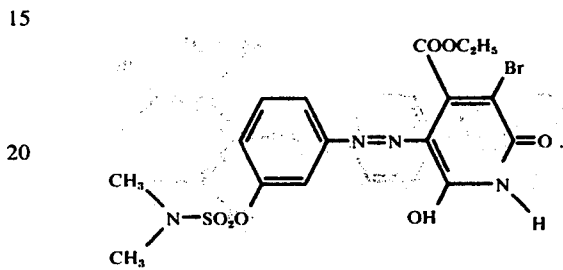


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25. The compound according to claim 6 having the formula



26. The compound according to claim 6 having the formula



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